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Investigation of Photopolymerization Process

First Quarterly Report

15 NOVEMBER 1961 - 14 FEBRUARY 1962

Signal Corps Contract DA 36-039-sc-88933

File Number 00528-PM-62-91-91 (2350)

PR & C Number 62-ELS/R-2350 (61/2355)

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Binghamton, New York

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General Aniline & Film
Corporation
Ansco Division
Binghamton, N. Y.

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"Investigation of the Photopolymerization Process"

First Quarterly Report

15 November 1961 - 14 February 1962

Object: To conduct a research investigation of photopolymerization techniques and their utilization as a dry picture-taking and printing medium for military use.

Signal Corps Contract No.: DA 36-039-sc-88933
File No.: 00528-PM-62-91-91 (2350)
PR & C No. 62-ELS/R-2350 (61/2355)

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<p>ANSCO, Division of General Aniline & Film Corporation, Binghamton, N. Y.</p> <p>Investigation of the Photopolymerization Process - E. Cerwonka</p> <p>First Quarterly Progress Report, 15 Nov. 1961 to 14 February 1962 Signal Corps Contract DA 36-039-sc-88933 File No. 00528-PM-62-91-91 (2350) - Unclassified Report</p> <p>Azohydroperoxides reported in the literature require relatively long exposures in photopolymerizable</p>	<p>ANSCO, Division of General Aniline & Film Corporation, Binghamton, N. Y.</p> <p>Investigation of the Photopolymerization Process - E. Cerwonka</p> <p>First Quarterly Progress Report, 15 Nov. 1961 to 14 February 1962 Signal Corps Contract DA 36-039-sc-88933 File No. 00528-PM-62-91-91 (2350) - Unclassified Report</p> <p>Azohydroperoxides reported in the literature require relatively long exposures in photopolymerizable</p>
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INVESTIGATION OF THE PHOTOPOLYMERIZATION PROCESS

A. PURPOSE

The general objective of this research contract is to conduct an investigation of photopolymerization techniques and their utilization as a dry picture taking and printing medium for military use. Detailed requirements are contained in "Technical Guidelines for PR & C No. 62-ELS/R-2350 (61/2355)", dated 11 May 1961.

B. ABSTRACT

Azohydroperoxides reported in the literature require relatively long exposures in photopolymerizable layers and show poor stability in coatings. However, a water-soluble compound of this group has been prepared, and its light sensitivity warrants further evaluation as a photoinitiator. Photopolymerizable coatings containing hydroxyethylcellulose as binder in place of gelatin require much less exposure in ferric salt and silver halide catalyzed systems. Free radical reactions in coated layers may be detected by means of indigocarmine. In a variation of the catatype process applied to photopolymerizable coatings it has been found that latent image silver produced during exposure was insufficient in concentration to inhibit polymerization to a noticeable degree. Ceric oxalate-monomer formulations appear to be pH dependent in regard to stability. An emulsion coating containing as its hydrophilic phase a dispersed water-soluble monomer along with polyethylene glycol produces a photopolymerizable dry print-out system.

C. PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

1. The following reports were issued:

- a. Monthly Report No. 1: "Investigation of the Photopolymerization Process"; 15 November - 14 December 1961
Author: Edward Cerwonka
- b. Monthly Report No. 2: "Investigation of the Photopolymerization Process"; 15 December 1961 - 14 January 1962
Author: Edward Cerwonka

2. The following lecture was given on Thursday, 18 January 1962, at Little Silver, N. J., before the local A.C.S. and S.P.S.E. Chapters:

"Polymeric Photographic Systems"
Steven Levins

3. The following conferences were held:

- a. 8 December 1961
- b. 19 January 1962

Both meetings were held at the U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, and were attended by Ansco staff members and representatives of the USASRDL. Research progress was reviewed.

D. FACTUAL DATA

1. Azohydroperoxides as Photopolymerization Catalysts

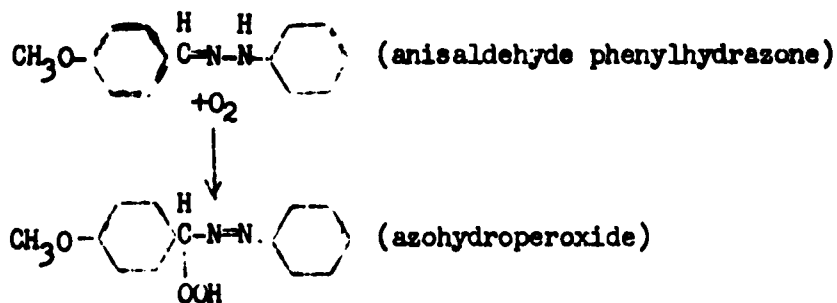
The azohydroperoxides, also known as Busch peroxides (1,2) have not previously been applied to photoreproduction processes. Stoltzenberg (3) noted that the azohydroperoxide derived from the p-tolyldrazone of anisaldehyde photopolymerized styrene.

a. Anisaldehyde Phenylhydrazone Azohydroperoxide

The azohydroperoxide derived from anisaldehyde phenylhydrazone was selected for tests to furnish information as to the light exposure required in coatings and as to the stability.

Preparation: Anisaldehyde phenylhydrazone (3 grams, m.p. 121°C, recrystallized from methanol) was dissolved in anhydrous benzene (300 ml). Oxygen was bubbled into the rapidly stirred solution at room temperature for a period of three hours. Evaporation of the solvent under reduced pressure yielded 3.1 grams of a yellow solid which darkened if allowed to remain in white light. The product was recrystallized from n-hexane (800 ml). Yield 2.9 grams, m.p. 83-84°C.

analysis: carbon, calc'd. 65.2%, found 64.9%. Hydrogen, calc'd. 5.45%, found 5.89%. Nitrogen, calc'd. 10.85%, found 10.49%.



The compound is insoluble in water, but dissolves in most organic solvents. A methanol solution was prepared with concentration of 1 mg per ml and found to transmit as follows in visible light:

22% at 400 mμ
80% at 540 mμ

Photopolymerization solution experiments were carried out to compare the induction period of this compound with that of iron peroxide and of a light-sensitive dye. In each case the photosensitive solution was added to 5.0 ml of A-5 and then exposed to the light from a 1000-watt tungsten lamp at 23 inches, the solution being stirred magnetically.

TABLE I.

<u>Photocatalyst</u>	<u>Induction Period</u>
Azohydroperoxide (10 mg) in 1.0 ml methanol	2 minutes 27 seconds
Ferric ammonium oxalate (24.7 mg) in water (1.0 ml) plus aqueous hydrogen peroxide (1.0 ml of 1%)	50 seconds
Riboflavin (1.0 ml of 0.1% aq.)	3 minutes 27 seconds

Thermal polymerization was effected by heating a solution of A-5 (5.0 ml) with azohydroperoxide (10 mg in 1.0 ml methanol) to a temperature above 84°C.

Some evidence as to stability was found by testing the ability of a methanol solution of azohydroperoxide to cause photopolymerization after the lapse of several days. Part of a solution containing 100 mg azohydroperoxide in 10 ml absolute methanol was kept in the cold room (0°-5°C) shielded from light, and the remainder was preserved at room temperature. A one ml sample was added to 5.0 ml A-5 at the time the solution was prepared and at later dates to compare the induction periods.

TABLE II.

Induction Period Change with Storage

	<u>Three Days</u>	<u>Five Days</u>	<u>Seven Days</u>	<u>Twelve Days</u>
Sample Stored in Dark Room	3:22	3:30	3:30	3:30
Sample Stored at 0°-5°C	2:27	2:30	2:30 (not taken)	

The induction period observed with the freshly prepared sample before it was divided for the test was 1 minute 45 seconds.

A sample of the material (0.5 gram) was dissolved in dibutyl phthalate (5 ml), then dispersed in a gelatin solution containing A-5 (6.0 ml). After the dispersion had been coated on paper base and dried, it was exposed for 30 seconds to the light from a 375-watt reflector lamp at 16 inches. After washout of the unpolymerized areas with warm water, a yellow-colored resist was obtained which darkened in color as the processed sample continued to age.

Other formulations of the same azohydroperoxide were prepared in which the weight of light sensitive material was varied (0.1 g to 2.0 g). Methanol, Carbowax, and benzene were tried as solvents for the azo compound. In all preparations coated, an exposure of thirty seconds or more was required to produce a resist after washout.

When a coating was exposed after several day's storage, no photoresist could be obtained. One sample (#0039) stored under refrigeration for a week gave a resist after longer exposure (two minutes).

Substitution of azohydroperoxide for cumene hydroperoxide in an iron salt A-5 coating gave a composition requiring three seconds exposure. Since the azo compound is less stable than the cumene hydroperoxide, nothing was gained by the substitution.

Although the stability of these coatings was poor, the purified product does not apparently deteriorate if kept in the cold and shielded from light. As noted before, methanol solutions preserved in this way are also stable.

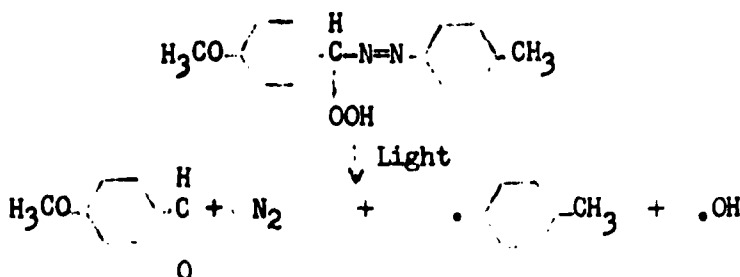
b. Other Azohydroperoxides

Several other azohydroperoxides were prepared following the procedure described for the synthesis of that derived from anisaldehyde phenylhydrazones. Data are summarized in the following table.

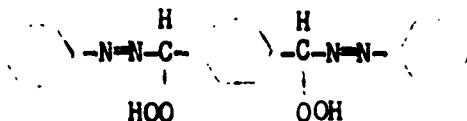
TABLE III.

<u>Hydrazone</u>	<u>M.P., °C</u>	<u>M.P. of Azohydroperoxide °C</u>
anisaldehyde phenylhydrazone	121	83-84
anisaldehyde p-tolylhydrazone	126	56-57
p-hydroxybenzaldehydephenylhydrazone	177	product not pure
terephthalaldehyde bisphenylhydrazone	260	no oxygen absorbed
p-dimethylaminobenzaldehydephenylhydrazone	122	77-78

It was decided to attempt preparation of a dihydroperoxide from the terephthalaldehyde bisphenylhydrazone in the hope that photodecomposition of the product might yield two hydroxyl radicals instead of the one obtained by photodecomposition of the monophenylhydrazones.



The above equation is given by Stoltzenberg (3).



Proposed bisazohydroperoxide from terephthalaldehyde bisphenylhydrazone

The fact that only starting material could be recovered suggests that the second phenylhydrazone substituent behaves like a nitro or other electronegative group. As noted in the literature (2,3) the presence of such groupings in the phenylhydrazone molecules inhibits the oxygen uptake of the compound. For this reason carboxylic or sulfonic acid derivatives of azo hydroperoxides apparently do not exist.

This situation does not, however, rule out the possibility of azohydroperoxides made soluble in aqueous acid by reason of the presence of amino or substituted amino

groups in the molecule. The p-dimethylaminobenzaldehyde derivative listed in Table III, using the procedure already given, was prepared without difficulty. It is insoluble in water as the free base, but is easily soluble in dilute hydrochloric acid. Tests show that the pure material quickly darkens in light. Photopolymerization of A-5 by the material is accelerated in acid solution. As yet, no attempt has been made to coat the material on a support.

2. Hydroxyethyl Cellulose as Binder in Photopolymerizable Layers

Based on work carried out in October, 1961, we recently filed a patent disclosure, AD 1752, "Method of Preparing Colored Photoresists using Leuco Dyes". Herein is described a preparation of leucomethylene blue in aqueous solutions. Methylene blue solution (10 ml. - 37 mg) was found to be decolorized when 274 mg ferrous ammonium sulfate and 500 mg disodium versene were added. The solution, however, was found to undergo rapid oxidation to the colored form by so-called "inert" gelatin. A large amount of additional ferrous salt was found to be required for the reduction of the dye back to its leuco form. When hydroxy ethylcellulose ("Natrosol" - Hercules Powder Co.) was substituted for the gelatin, the leuco dye was not oxidized. It is possible that inert gelatin retains traces of peracetic acid used in removal of organic sulfides and other reducing substances.

a. Ferric Salt Coatings with Hydroxyethyl Cellulose

When ferric ammonium oxalate and A-5 solution were coated on paper base, using hydroxyethyl cellulose as binder in place of gelatin, it was found that less exposure was required to produce a resist after peroxide wash. With a 375-watt reflector lamp at sixteen inches, the exposure required was .06 seconds, as compared to the 1.5 seconds average requirement for a ferric ammonium oxalate, A-5, Atlantic gelatin coating. Comparison of test strips exposed through a 2 step-wedge confirmed this observation. No additional "speed" was attained by addition of dextrose-versene or bisulfite-versene to the coating formulation.

A test strip of the "fast" coating was exposed in a Graflex camera and gave a visible photoresist under the following exposure conditions: aperture: f/4.7; object six feet from lens; two 400 watt-candlepower lamps four feet from object; time of exposure -- 8 minutes. (All Weather Pan requires 1/25 second under the same conditions).

Ferric salt, A-5 coatings prepared with the cellulose derivative as binder are stable at least a week at room temperature. Results of storage for longer periods will be reported later.

A variation of the ferric ammonium oxalate, A-5 photopolymerizable composition consists in dispersing cumene hydroperoxide in the coating solution. Exposure of a test strip so prepared through a $\sqrt{2}$ step wedge showed an increase in speed over gelatin coatings. Required exposure time was reduced from 3 seconds to .06 second. Coatings containing the organic hydroperoxide, however, were found to develop a layer of polymer within a few days when stored at room temperature.

b. Silver Halide Coatings

A marked increase in photopolymerization speed was observed when the coating speed of silver bromide, A-5 in hydroxyethyl cellulose was compared with that of the silver bromide, A-5, gelatin formulation. Silver nitrate (3.0 g) and potassium bromide (1.65 g) were chosen in a ratio of about 17.7 millimoles silver to 13.9 millimoles bromide for each coating. Exposure of a test strip of the gelatin coating (#0031) through a $\sqrt{2}$ step wedge for one minute showed polymer only in the step of maximum light transmission. The hydroxyethylcellulose sample (#0039) extended to the step corresponding to optical density = 2.00 on the silver wedge. The relative exposures required to the light from a 375-watt reflector lamp at 16 inches were about 40 seconds for the gelatin coating and 0.6 second for the hydroxyethylcellulose coating.

Silver bromide, A-5, hydroxyethyl cellulose coatings have not shown dark polymerization in a week of storage.

Washout of test strips of this coating was carried out, following minimum exposure, in (a) nitrogen-flushed water and (b) oxygen-flushed water. The resist, a letter image, appeared identical. This result is in accord with the probable formation of polymer during light exposure in the case of this photocatalyst, rather than during the washing step.

When the molar ratios of bromide to silver were reversed (17.7 mmoles bromide to 13.9 millimoles silver) exposure of coated strips (#0038) showed no photoimage produced during periods of .06 to 60 seconds. With the excess silver ion ("print-out" formulation) polymer formation seems to accompany the appearance of print-out image.

c. Photoreducible Dye Coatings

Polymerization induced by the photoreducible dye, methylene blue, was initiated by shorter exposures when the hydroxyethyl cellulose binder was substituted for gelatin. The coating formulation (#0025) included methylene blue (37 mg), disodium versene (500 mg), A-5 (6 ml) and Natrosol (2.5 g) mixed with 45 ml deionized water. Exposure of 25 to 30 seconds with the reflector lamp at a distance of 16" produced a resist after water wash. Gelatin coatings required exposure of at least one minute, using the same exposure conditions.

3. Color Changes Resulting from Free Radical Formation

a. Indigo Carmine as an Indicator of Free Radical Formation

It is reported (4) that indigo carmine (indigo 5,5' disulfonic acid) is rapidly oxidized by hydroxyl radicals. Our experiments showed that this water-soluble dye is not affected by ferrous or ferric ion, and is only slowly attacked by aqueous hydrogen peroxide. The combination ferrous salt-peroxide, however, decolorizes the dye almost immediately. It seemed of interest, therefore, to examine the possible application of this dye as an indicator of the presence of free radicals in coated layers.

A solution of ferric ammonium oxalate, cumene hydroperoxide and indigo carmine was prepared in gelatin and coated on paper base. An exposure through a negative for five seconds to the 375-watt reflector lamp at sixteen inches gave no perceptible color change. When, however, the coated surface was moistened slightly with a sponge, the light-exposed areas showed up as white letters. Steam produced a similar bleaching effect. The result would indicate that the application of moisture permits interaction of ferrous ion with organic hydroperoxide in the coated layer, accompanied by free radical release.

A paper base coating of indigo carmine and the azohydroperoxide derived from anisaldehyde phenylhydrazone (no monomer present) was given an exposure of three minutes to the usual light source. This resulted in bleaching of the exposed areas. The blue color of the dye was not regenerated in air as is the case with the photo-produced leucomethylene blue.

Thermally-produced free radicals also effect the bleaching of indigo carmine. This was demonstrated by heating to 70°C a paper base test strip coated with azobisisobutyronitrile and indigo carmine in a gelatin binder. It is well known that azobisisobutyronitrile begins to dissociate into free radicals at 70°C and that polymerization of vinyl monomers can be initiated in this manner.

No rapid dry photo process has as yet been derived from these reactions. The photobleaching of indigo carmine by an azohydroperoxide is a slow process. Azobisisobutyronitrile produced no photoresist in a coated layer after five minutes exposure to visible light. It would seem to be more suited to a thermographic process.

b. Color Reaction Involving Azobisisobutyronitrile

One formulation was prepared to test this idea. It comprised ferric ammonium oxalate, cumene hydroperoxide, A-5, azobisisobutyronitrile and malachite green, coated on paper base. When a dried strip was exposed for five seconds to the usual light source, no change was evident. However, when the test strip was heated in an oven at 70°C for a period of twenty minutes, a darkened image appeared in the exposed areas, whereas the unexposed areas became a light green. After continued exposure of the processed strip to room light for a period of weeks, the color of the "unexposed" areas darkened. If either the organic hydroperoxide or the azo compound was omitted from the formulation the dark image was not produced after exposure and heat.

Changes in the formulation have not reduced the required light exposure.

4. Metallic Silver-Hydrogen Peroxide as a Polymerization Inhibitor

The Gros patents (5) describe a process by which a reversal image transfer is effected. When a silver negative is immersed in an ethereal solution of hydrogen peroxide, there is an adsorption of the peroxide to clear areas on the negative. Catalytic decomposition of the peroxide takes place in proportion to the density of the silver areas. The negative is withdrawn from the peroxide after an unspecified period and placed in contact with a receiver layer containing ferrous salt and gelatin. This permits a peroxide-ferrous reaction, the result being an "image-wise" production of ferric ion, accompanied by insolubilization of gelatin where ferric ion is formed. Washout reveals a water-insoluble image which is a reversal of the silver image on the negative. (The

term "catatype" is properly restricted to Gros' process in which manganous salts are employed in place of ferrous.)

During the period September-October, 1961, tests showed that the transfer process was improved by incorporating A-5 in the receiver layer. Certain organic developers could replace the ferrous salt in the receiver layer. Those found satisfactory were hydroxylamine hydrochloride, metol, amidol (2,4 diamino phenol dihydrochloride). Later tests added thiourea and ascorbic acid to the list. Hydroquinone was not suitable in the reaction, nor was p-phenylenediamine dihydrochloride. There was no catalytic decomposition by silver of organic hydroperoxides or peroxides, so far as could be determined.

The density of silver produced by exposure of a print-out emulsion is, of course, quite small in comparison with that present on a developed negative. Nevertheless, exposure of a print-out emulsion for three minutes to the light from a 375-watt reflector lamp at sixteen inches produces a silver density that suffices for the peroxide decomposition. A test strip so exposed was dipped in ethereal hydrogen peroxide for a few seconds, dried, and placed on a receiving layer (paper base) consisting of amidol and A-5 gelatin. Washout with warm water showed a resist on the paper base which was a reversal of the print-out image.

In another test a silver azide emulsion (6) was coated on paper base. The print-out image obtained by exposure did not decompose hydrogen peroxide catalytically.

As a further variation, the effective reagents--monomer and reducing agent--were added to a photographic emulsion and coated as a single layer on paper base. Certain of the reducing agents used in the transfer layer were ruled out as emulsion additives. Ferrous salt reduces silver halide to metallic silver if present in the emulsion. Thiourea in the concentration required for the redox reaction was found to convert the silver halide in the emulsion into a light-insensitive complex. Ascorbic acid was selected for the single layer coatings, since it does not reduce unexposed silver in its acid form, and since it induces polymerization of A-5 in the presence of hydrogen peroxide.

By adding ascorbic acid and A-5 to "Ampan" (a bromo-iodide emulsion) and coating on paper stock (#9966), a layer was obtained which prior to exposure polymerized when dipped into ethereal hydrogen peroxide. When the test sample was exposed through a negative for five minutes to the customary light source, sufficient silver was produced to inhibit the polymerization process. A few bubbles of gas arose

from the print-out areas during the ethereal peroxide immersion. A warm water wash (40°C) showed that a resist had formed in the unexposed areas. The exposed areas were denoted by "troughs", containing print-out silver. Removal of the silver with bleach showed that these troughs extended to the paper base. Shorter exposures (less than five minutes) produced no discernible "troughs" but only a continuous polymer layer after bleach-out of the silver.

These results indicate that considerable silver must be generated before enough hydrogen peroxide is decomposed to make a differentiation possible between exposed and unexposed areas. It will therefore be necessary to develop the silver before peroxide decomposition, in order to achieve a faster system.

Work on this problem is being continued by Mr. Ray Rice of the Ansco Laboratories.

5. Stabilization of Ceric Salt Compositions

Earlier reports (1960-1961) have indicated the desirability of a stable photosensitive ceric or manganic salt composition. In visible light ceric ion decomposes oxalate ion, accompanied by the liberation of a carbon dioxide radical-ion. Polymerization in a coated layer may therefore be more efficient in the ceric-catalyzed process. The difficulty lies in the slow dark reaction of ceric ion with oxalate ion, thus limiting the coating stability.

Replacement of versene disodium salt for oxalate in a ceric ion, A-5 coating was found to increase the stability of the layer. The exposure required to give a resist, however, was increased from three seconds to thirty seconds (#9963, #9968).

Introduction of small concentrations of copper salt has given a similar result—stability but longer exposure (five minutes) required. (Samples #0043, #0046.)

Photopolymerizable compositions containing ceric ions appear to be strongly pH dependent. For example, it has been found that solutions of ceric ammonium nitrate, oxalic acid and A-5 polymerized in red light within a few minutes. On the other hand, solutions of ceric ammonium nitrate, potassium oxalate and A-5 are stable in red light for at least 4 hours. Control of pH may therefore become a means of stabilizing ceric ion coatings.

6. Dry Photopolymer Print-out Process

It has been observed that the addition of water-soluble polyethylene glycol (Carbowax 600) to a photopolymerizable solution (ferric ammonium citrate, methylene bisacrylamide, cumene hydroperoxide, water) produces a highly opaque white precipitate at the moment of polymerization.

The reaction is independent of the photoinitiator system used. Similar results are obtained with photoreducible dyes or the ceric ammonium nitrate-oxalic acid system as a photoinitiating Redox system. It has also been shown that the reaction is independent of the molecular weight of the polyethylene glycol added; in fact, Carbowax compounds of the general formula $\text{ROCH}_2(\text{CH}_2\text{OCH}_2)_x\text{CH}_2\text{OH}$ of an average molecular weight of 190 to 3700 behave identically. Furthermore, a variety of compounds, based on the hydroxyethyl backbone ($-\text{CH}_2\text{CH}_2\text{OH}$), such as Cellosolve, Carbitol, Pluronic, etc., can be substituted for Carbowax.

Cross-linking of the vinyl monomer with polyethylene glycol was first advanced as an explanation for the formation of the white precipitate. This seems improbable, as Dr. F. W. Millard of the Photo Repro Group has examined the infrared spectra of polymeric N,N' methylene bisacrylamide formed in the presence of polyethylene glycol. He finds no structural change indicated. Therefore, the incompatibility of the polymer formed in polyethylene glycol and its precipitation out of the solvent seems at the present the best explanation of the effect described.

When coatings of the above composition are made on clear film base, a very faint milky precipitate is obtained on exposure.

This faint image can be effectively increased in density and contrast when the coating is steamed, after exposure, with water vapor. It is concluded that the presence of water is necessary to obtain the effect and that an emulsion coating containing as its hydrophilic phase a dispersed water-soluble monomer plus polyethylene glycol may produce a photopolymerizable dry print-out system.

A typical coating formulation is the following:

Aqueous Phase

Carbowax 600	6.0 g
Cumene hydroperoxide	0.1 g
A-5	7.0 g
Glycol	2.0 g
Ferric ammonium oxalate 36%	0.4 g

10 cc of the above solution are dispersed in

Oily Phase

Ethylcellulose T10	50 g
(10% toluene solution)	1 g
Span 20	1 g
Dibutyl phthalate	1 g

Coatings on cellulose triacetate, after evaporation of the solvent are non-tacky and glass-clear. When exposed through a lettered negative to a 375-watt reflector lamp at a distance of 10 inches, a highly opaque white image appears in 2-4 seconds which does not increase further in density. The image exhibits a slight yellow stain (due possibly to the presence of ferric salt) when such a ferric salt-cumene hydroperoxide system is used as a photoinitiating redox system.

The process described is a true dry process; no vaporizing, heat washout, or wet processing is required to obtain a strong white image. The process is a positive process, inasmuch as the white image is produced in the exposed areas, whereas the unexposed areas appear dark, especially when coatings are made on black paper.

In the case of ferric ammonium oxalate used as photoinitiator, the coating is mainly sensitive to ultraviolet and blue light. Protection of the exposed strip is, therefore, best accomplished by dipping it in an ultraviolet absorbing solution, e.g., a 1% solution in toluene of 2(2'-hydroxy 5'-methylphenyl) benzo-triazole. (Tinuvin-P, Geigy)

Present investigations are continuing to determine the speed and gradation characteristics of this dry photopolymer process. A patent application for the above referenced process is in preparation.

References

- (1) M. Busch & W. Dietz, Ber. 47, p. 3277 (1914)
- (2) K. H. Pausacker, J.C.S. (1950) p. 3478
- (3) D. J. Stoltzenberg, Thesis, Technische Hochschule, Karlsruhe (1958)
- (4) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions", D. Van Nostrand Co., Inc., Princeton, N.J. (1961)
- (5) O. Gros, DRP 147, 131; DRP 157, 411
- (6) Y. Tomoda, "Print-Out Emulsion with a Component of Silver Azide" Photo. Sci. and Eng. Vol. 4 No. 4, pp. 196-8

E. PROGRAM FOR NEXT INTERVAL

1. Emphasis will be placed on studies involving speed increases obtained by the use of hydroxyethylcellulose binder. Other non-gelatin binders will also be evaluated.
2. The speed and gradation characteristics of the dry process based on the use of catalyst, monomer and Carbowax will be investigated and experiments undertaken to improve them.
3. Studies of the pH dependence of the ceric catalyst system will be continued.
4. Photopolymerizable compositions containing water soluble azohydroperoxides will be prepared. Exposure requirements and stability will be determined.
5. Further investigations will be made on color producing free radical reactions, especially in non-gelatin type binders.

F. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

<u>Levinos, Steven</u>	Project Manager
Education:	Polytechnic Institute of Brooklyn, Brooklyn, N. Y. B. S. in Chem. 1937
Employment:	Co-owner, Smith Chemical Works, Edgewater, N. J. 1936-1938 Ansbacher-Siegle Corporation Staten Island, N. Y. National Bureau of Standards, Washington, D. C. 1942- 1947 Research Chemist Signal Corps Engineering Laboratories, Fort Monmouth, N. J. 1948-1955 Chief, Photographic Branch Photo & Repro Group, GAF Corpo- ration, Binghamton, N. Y. 1956- Research Manager, Rapid Access Recording Systems
Research Fields:	Pigments, radiochemistry, photo- graphic processes, photo- polymerization
Man Hours Devoted to this Project (15 November 1961 - 14 February 1962)	25
<u>Schwerin, Andre K.</u>	Research Manager, Photopolymer and Color Systems
Education:	University of Berlin (Germany) 1926 M. D. 6 years postgraduate work in Biophysics
Employment:	Biophysical Institute of University of Frankfurt (Germany) 1926-1930 Res. Physicist University Hospital U. of Berlin (Germany) 1930- 1932 Radiologist Paris (France) self-employed Chem. Lab. 1933-1939 Consultant

Forgeries de la Loire (Ironworks)
1940-1945 Res. Physicist
Nat'l. Council of Scientific Research - Paris (France)
1946-1948 Res. Assoc.
Montreal (Canada) self-employed -
Chem. & Phys. consultant for
Photography & Photoengraving
1948-1953
Phys. Institute Univ. of Montreal
1953-1956 Res. Associate
Ansco, Div. of GAF, Binghamton,
N. Y. 1956- Sr. Res. Specialist;
1961 - Research Manager, Photo-
polymer and Color System

Research Fields:

Radiology, Dosimetry of X-radiation,
Colorimetry, Spectrophotometry,
Printing Process, Nuclear,
Emulsions, Polymer Chemistry,
holds 8 U. S. Patents

Man Hours Devoted to
this Project (15 November
1961 - 14 February 1962)

25

Cerwonka, Edward

Senior Research Chemist

Education:

Fordham University Ph. D. 1952
Organic Chemistry

Employment:

U. S. Testing Co., Hoboken, N. J.
1952-1953 Res. Chem.
U. S. Testing Co., Boston, Mass.
1953-1954 Res. Chem.
Metaelectro Corp., Laurel, Md.
1954-1957 Sr. Res. Chem.
Ansco, Div. of GAF, Binghamton,
N. Y. 1957 Sr. Res. Chem.

Research Fields:

Radio isotopes as Tracers,
Synthesis of radio active
organic compounds, Synthesis
of organic nitrogen compounds,
polymer chemistry.

Man Hours Devoted to
this Project (15 November
1961 - 14 February 1962)

504

We draw on other members of our Research staff for occasional consulting services:

Dr. F. W. H. Mueller, Director of Research and Development

Dr. F. J. Kaszuba, Associate Director of Research and
Development

Dr. H. F. Nitka, Associate Director of Research and
Development

Dr. G. A. Wieseahn, Research Librarian

As provided under the contract, Dr. Norman G. Gaylord has been retained as a consultant on this project.

The Accounting Dept. Report on this Project will be submitted by the Federal Sales Dept. within 30 days.

A handwritten signature in cursive script, reading "Steven Levins".

Steven Levins
Project Manager

HEADQUARTERS
U. S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY
FORT MONMOUTH, NEW JERSEY

SIGRA/SL-SA

Contract No. DA 36-039-sc-88933
Report No. First Quarterly
Project Engineer: Miss M. Levy

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